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Small-Angle Neutron Scattering from Nonuniformly Labeled Block Copolymers

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ABSTRACT: An analytical expression for the scattering profiles from a disordered melt of symmetric, nonuniformly labeled A−B diblock copolymers is derived using the multicomponent random phase approximation. The expression is simple and contains one additional, temperature-independent constant that is a measure of the ensemble-averaged deviations of the scattering lengths of the two blocks from their mean values. The kind of nonuniformity considered here is a natural consequence of many of the popular synthetic routes used to obtain deuterium labeled block copolymers. Small-angle neutron-scattering experiments were conducted on a block copolymer obtained by saturating the double bonds of an anionically synthesized polydiene precursor with deuterium. The scattering data from our block copolymer in the disordered state are qualitatively inconsistent with all of the previously published theories on block copolymer thermodynamics. The data are, however, in quantitative agreement with the proposed expression. This enables a quantitative estimate of the nonuniformity of the deuterium labels in the sample. Our work also enables a new measure of the chain dimensions of block copolymers, one that is not dependent on the location of the scattering peak that arises due to the connectivity of the blocks.

Introduction

Deuterium labeling is widely used in the study of the structure and thermodynamics of polymer systems such as polymer solutions and blends, linear and branched block copolymers, and complex multicomponent mixtures containing homopolymers and copolymers.[1−19] The properties of these systems are probed by a variety of techniques such as small-angle neutron scattering (SANS), deuterium NMR, IR dichroism, and light scattering. In most cases (e.g., refs 1−19), it is assumed that the deuterated polymer chains are uniformly labeled, i.e., each repeating unit contains a fixed number of deuterium atoms. This is not exactly true. The purity of deuterated monomers is seldom better than 99%. Polymer samples made by polymerizing these monomers comprise many different kinds of copolymer chains with sequences of deuterated monomers interrupted by a few hydrogenated monomers at random locations. It is often convenient and cost-effective to make deuterated polymers by first making a hydrogenous polymer and then adding deuterium labels by post-polymerization chemical reactions. One can, for example, make deuterium-labeled polyolefins by saturating the double bonds of a hydrogenous polybutadiene sample with deuterium gas.[1−20] In the absence of side reactions, two deuterium atoms would be added on to each butadiene monomer, and all of the polyolefin chains would be uniformly labeled. However, side-reactions lead to the addition of a significantly larger number of deuterium atoms per monomer (typically 3). It has been established that this leads to nonuniformly labeled polyolefins.[3−8,12−13] Nonuniformly labeled polymers can, in some cases, be obtained by simply dissolving the polymers in an appropriate medium. For example, water-soluble polymers such as polyacrylamide and proteins undergo H−D exchange in D_2O.[21] Similar exchange reactions take place when polyethylene is exposed to deuterium gas under appropriate conditions.[22] The statistical nature of the H−D exchange leads to an ensemble of nonuniformly labeled polymers even in cases where the starting materials (e.g., proteins and D_2O) are perfectly uniform.

A small amount of nonuniformity often enables measurements that are not possible in its absence.[23−25] For example, the structure factor, S, from a melt composed of uniformly labeled homopolymers is identically zero at all scattering vectors, q. SANS measurements on uniformly labeled samples thus provide no structural information. However, for the case of nonuniformly labeled homopolymers that are otherwise monodisperse, $S(q)$ is proportional to the Debye function characterizing the individual chains.[25] Measurements of the chain dimensions in these systems are thus enabled entirely due to the nonuniformity of the labels. Similar effects are seen in dynamic measurements, e.g., in the measurement of diffusion coefficients. The translational diffusion coefficient of block copolymer chains in solution can, in some cases, be measured by a simple dynamic light scattering (DLS) experiment.[23,24] The reason for this observation is the small but finite nonuniformity in composition of anionically synthesized block copolymer chains.[23] If the block copolymer chains were perfectly monodisperse then only collective and internal modes would be observed by DLS.[23]

In this paper, we derive an expression for the structure factor of a diblock copolymer melt composed of nonuniformly labeled chains, using the multicomponent random phase approximation (RPA). We demonstrate

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Table 1. Characterization of Polybutadienes

polymer	$\bar{M}_w$ (kg/mol)	PDI[a]	% 1,2[b]	ρ (g/mL), 23 °C	n_D (per C_4)[c]
homopolymer A, hPB[90]	10.1	1.01	89	0.8625	0
homopolymer B, dPB[63]	9.9	1.02	62	0.9125	3.44
block A of A−B diblock	41.3	1.01	92	NA	NA
block B of A−B diblock	37.6	1.01	63	NA	NA
overall A−B diblock, dPB[90]-dPB[63]	78.9	1.01	78	0.9098	2.99

[a] Polydispersity index. [b] Percentage of 1,2 units in polybutadiene precursor. [c] Average number of deuterium atoms per C4 repeat unit.

the validity of our derivation by comparison with experiments. This work may be regarded as an extension of a previous work in ref 25, where the structure factor of nonuniformly labeled homopolymer blends was studied.

There is considerable interest in the configuration of block copolymer chains, especially in the vicinity of the order−disorder transition.[26] The standard method of obtaining this information is by comparing the measured structure factor of the copolymer in the disordered state using either SANS or small-angle X-ray scattering (SAXS) and comparing it to the theoretical predictions of Leibler.[27] For perfectly monodisperse diblock copolymers, the parameter that describes the block copolymer chain configuration is the average statistical segment lengths of the two blocks, which can be obtained from the location of the peak in the diblock structure factor that arises due to the connectivity of the blocks. It is often found that the statistical segment lengths thus obtained are significantly larger than those obtained from the same chains in either a homopolymer melt or in a blend with another compatible homopolymer. In other words, the structure factor peak seen in diblock copolymer melts is often not at the location that one would predict based on well-established statistical segment length data for the homopolymer chains. To our knowledge, there is no independent way of ascertaining whether the chains are truly stretched or whether the relationship between the structure factor peak and the statistical segment length based on Leibler's theory is not accurate. The theoretical treatment that we develop in this paper enables determination of the statistical segment length of a block copolymer without relying on the location of the structure factor peak.

Experimental Methods

Polybutadiene was synthesized via anionic polymerization in hexane at 0 °C, using tetrahydrofuran (THF) as a polar additive to control the percentage of 1,2- vs 1,4-addition. All reagents were purified under high vacuum. A trial-and-error method was employed to develop a calibration curve for the dependence of the percent 1,2- and 1,4-addition on initiator (*sec*-butyllithium) concentration and molar ratio of THF to initiator. A diblock copolymer of polybutadiene, with a different percent 1,2-addition for each of the blocks, was synthesized by sequential polymerization, in which the THF concentration in the reactor was adjusted after completing the polymerization of the first block. An aliquot of the first block (precursor) was isolated and terminated for characterization purposes, prior to the addition of the second block. The polymers were dried fully under vacuum at room temperature. They were then saturated (in solution in cyclohexane) using either hydrogen or deuterium gas in a Parr high-pressure reactor at 95 °C with a 5% palladium on barium sulfate catalyst. The polymers were again dried under vacuum at 150 °C for several days.

The molecular weights and architectures of the polymers were determined on a Waters 2690 gel permeation chromotography (GPC) system with a Viscotek triple detector. The three detectors (light scattering, viscometry, and refractometry) enabled the determination of the absolute number and weight-averaged molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and the polydispersity indices (PDI) of the homopolymers, the block copolymer precursor, and the block copolymer. The refractive indices of the polybutadiene/THF solutions are independent of the percentage of 1,2-addition in the range of our experiments; this simplification enables the characterization of the block copolymer. NMR spectroscopy was used to determine the percentage of 1,2- and 1,4-addition in all of the samples to an accuracy of ±1%. An aliquot of the precursor of the diblock copolymer was analyzed by GPC and NMR. The extent of 1,2-addition of the second block was then determined from the known molecular weight and monomer volume of each block and percentage of 1,2-addition of the first block.

The characteristics of the polymers used in this study are summarized in Table 1. Homopolymer A is a hydrogenated polybutadiene with 90% 1,2-addition {hPB[90]}, and homopolymer B is a partially deuterated polybutadiene with 63% 1,2-addition {dPB[63]}. The A−B diblock copolymer was obtained by deuterating a polybutadiene diblock copolymer with blocks comprising 90% 1,2-addition and 63% 1,2-addition, respectively {dPB[90]-dPB[63]}. The composition labels for our samples are based on our targets. Samples wherein the % 1,2-addition deviated more than 2% from the targets were discarded (see Table 1).

The densities of the polymers, ρ, at 23 ± 0.1 °C were measured using a density gradient column and are given in Table 1. The number of deuterium atoms per C_4 repeat unit, n_D, of each characterized polymer was obtained by comparing the densities of deuterated and hydrogenated polymer pairs obtained from the same polydiene precursor.

A binary blend of A and B homopolymers was created by dissolving the components in hexane followed by precipitation in a 50/50 mixture of methanol and acetone. After precipitation was complete (around 5 h), the polymer was collected and placed on a 1 mm thick quartz disk inside a 1 mm thick spacer with an inner diameter of 14 mm. The sample was heated in a vacuum oven at 150 °C for 2 days to ensure complete removal of solvent. A second quartz disk was then placed on top of the polymer. The sample was pressed together at high temperature and annealed for 10 min at 150 °C to erase the thermal history. After the sample was cooled to room temperature, glue was placed around the edges of the sample in order to prevent the sample from leaking out. The A−B diblock copolymer sample was encased between quartz windows using the procedure described above.

Small-angle neutron-scattering (SANS) experiments were conducted on the NG7 beamline at the National Institute of Standards and Technology in Gaithersburg, MD. The wavelength of the incident beam was 8.09 Å, and the detector-to-sample distance was 2.05 m. The raw data were converted to absolute coherent scattering intensity, I, as a function of q ($q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of the incident beam), after corrections for detector sensitivity, background, empty cell, and incoherent scattering were made, using standard procedures. For the binary A/B blend, corrections for the nonuniformity of deuterium labeling were made as indicated in ref 25.

The A/B blend and A−B block copolymer samples were studied as a function of increasing temperature (controlled to ±1 °C) from 29 to 200 °C (the high-temperature limit of the sample holder).

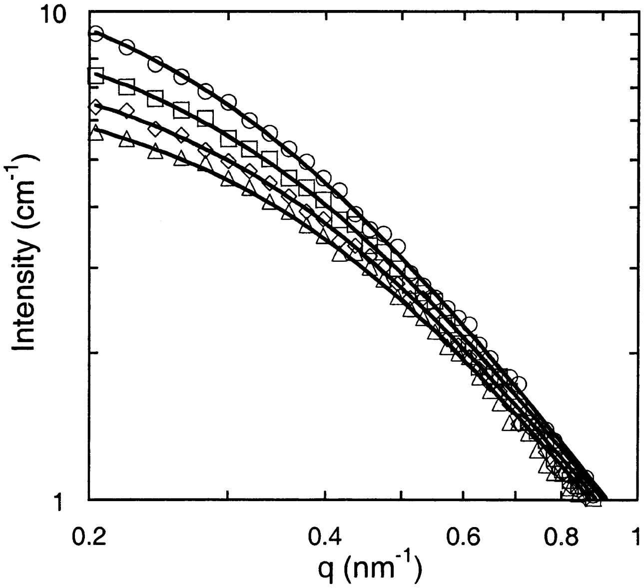

Figure 1. SANS intensity, *I*, vs scattering vector, *q*, obtained from the A/B binary blend. Solid curves are the random phase approximation for a binary blend fit to the data. The data were taken at the following temperatures: 29 (circles), 71 (squares), 113 (diamonds), and 154 °C (triangles).

Experimental Results

1. Binary Blend. The random phase approximation for a binary polymer blend is given by eq 1[28]

$$I(q) = \left(\frac{b_A}{v_A} - \frac{b_B}{v_B}\right)^2 \left(\frac{1}{N_A v_A \phi_A P_A(q)} + \frac{1}{N_B v_B \phi_B P_B(q)} - \frac{2\chi}{v}\right)^{-1} \quad (1)$$

where the Debye function, $P_i(q)$ is by definition

$$P_i(q) = \frac{2}{x_i^2}(\exp(-x_i) + x_i - 1) \quad (i = A, B) \quad (2)$$

b_i is the mean scattering length of each component, v_i is the monomer volume of each component, N_i is the number of repeat units of each component ($N_i = M_{w,i}/M_o$, where M_o is the monomer molecular weight), ϕ_i is the volume fraction of each component, and $x_i = q^2 R_{g,i}^2 = q^2 N_i l_i^2/6$, where l_i is the statistical segment length of each component. In this work, the reference volume v = 100 Å^3, which is roughly the volume of a C_4 repeat unit (the basis of each of the components).

In Figure 1, we show the measured coherent SANS profiles $I(q)$ from a 50/50 mixture of A and B homopolymers at selected temperatures. The curves through the data represent eq 1 with known values of N_i, v_i, and ϕ_i (the monomer volume was calculated based on the density of the polymer at 23 °C and its thermal expansion coefficient given in ref 29), and χ and l_i as the adjustable parameters. The statistical segment lengths of our components were previously reported in ref 30, where values l_A = 0.57 nm and l_B = 0.66 nm were obtained. It is well-known that the SANS profiles of polymer blends are insensitive to the statistical segment lengths of the individual components. Our adjustments of l_i were thus made in a manner that maintains the ratio $l_A/l_B = 0.57/0.66 = 0.86$.[30] The temperature dependence of χ and the statistical segment lengths obtained from the analysis of the A/B blend data are given in Table 2. Statistical segment lengths obtained from the fit are within 10% of the literature values.[30] The measured χ is nearly the same as that predicted from solubility parameters given in ref 13. The SANS data from the A/B blend are thus in good agreement with our expectations.

Table 2. Binary A/B Blend RPA Fit Parameters

T (°C)	χ_{AB}	l_A (nm)	l_B (nm)
29	0.0062	0.61	0.71
50	0.0054	0.60	0.70
71	0.0049	0.60	0.70
92	0.0043	0.60	0.70
113	0.0039	0.59	0.70
134	0.0037	0.60	0.70
154	0.0031	0.59	0.70
175	0.0028	0.59	0.69

2. Block Copolymer. The coherent SANS profile from a melt of perfectly monodisperse A–B diblock copolymer chains is given by[27]

$$I(q) = \left(\frac{b_A}{v_A} - \frac{b_B}{v_B}\right)^2 \left[\frac{S_{AA}^{\circ} + S_{BB}^{\circ} + 2S_{AB}^{\circ}}{S_{AA}^{\circ} S_{BB}^{\circ} - (S_{AB}^{\circ})^2} - \frac{2\chi}{v}\right]^{-1} \quad (3)$$

$$S_{ii}^{\circ} = \phi_i N_i v_i P_i(q) \quad (4)$$

$$S_{AB} = (\phi_A N_A v_A \phi_B N_B v_B)^{1/2} F_A(q) F_B(q) \quad (5)$$

$$F_i(q) = \frac{1 - \exp(-x_i)}{x_i} \quad (6)$$

where $F_i(q)$ is the well-known Leibler function, and the parameters b_i, v_i, N_i, ϕ_i, x_i, v and $P_i(q)$ have the same definition as in the blend case (eqs 1 and 2).

Some studies have concluded that both χ and the statistical segment lengths obtained in A/B blends and A–B diblock copolymers are different (e.g., ref 31). Others have reached the conclusion that χ obtained in the blends and block copolymers are within experimental error (e.g., ref 7). Thus, for the diblock copolymer case there are, in principle, 5 unknown parameters in the $I(q)$ expression (eqs 3–6): b_A, b_B, χ, l_A, and l_B. The homopolymer blend data analysis described above provides us with reasonable initial guesses of the values of the interaction parameter and the statistical segment lengths. Our first goal is thus to estimate b_A and b_B. We use a procedure that is similar to that given in ref 7. Equation 3 can be rewritten in terms of the structure factor of the diblock copolymer $S(q)$

$$I(q) = \left(\frac{b_A}{v_A} - \frac{b_B}{v_B}\right)^2 S(q) = CS(q) \quad (7)$$

We first examined the data obtained at the lowest temperature where the peak in $I(q)$ is most pronounced (29 °C). This data set is shown in Figure 2a. We used the value of χ obtained from our analysis of the A/B binary blend data, and changed the values of l_A and l_B obtained from the binary blend data by a constant multiplier α (α = $l_A/l_{A,ref} = l_B/l_{B,ref}$ where $l_{A,ref}$ = 0.61 nm, $l_{B,ref}$ = 0.71 nm) to match the theoretically predicted (eq 3) and experimentally measured location of the scattering peak. We then chose a constant C such that the theoretically predicted and the experimentally measured intensities at high q were the same. Note that uncertainties in χ do not affect the high-q portion of the SANS data.[27] This experimentally determined param-

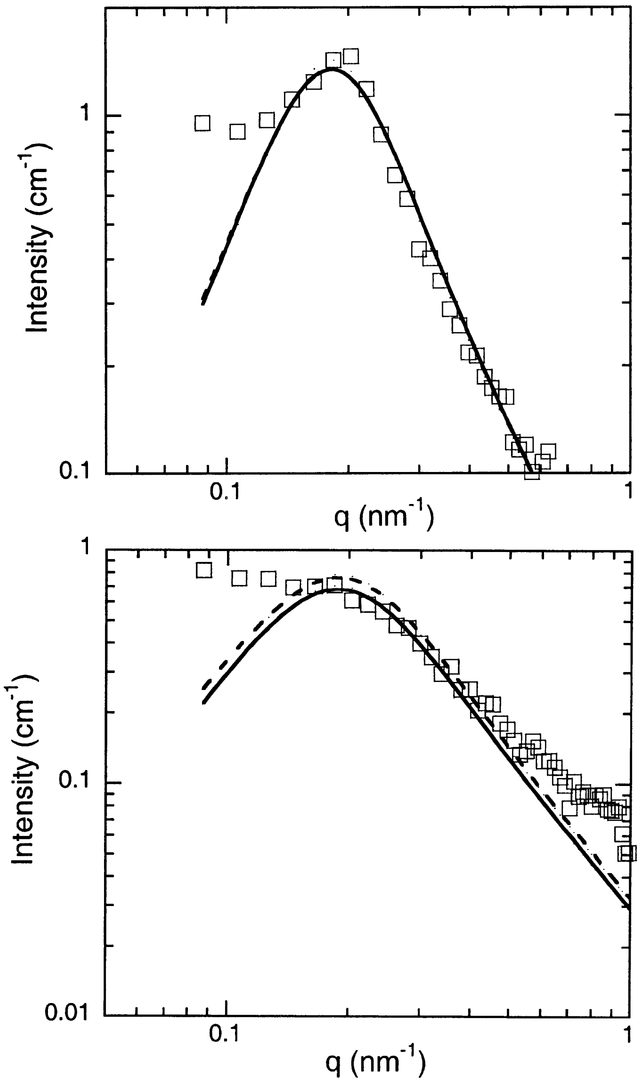

Figure 2. SANS data obtained at 29 (a) and 102 °C (b) from an A−B diblock. The solid curve is the random phase approximation for a diblock copolymer (Leibler) fit to the data. The dashed curve is the random phase approximation for a polydisperse diblock copolymer (Burger et al.) fit to the data. The dashed and solid curves are almost indistinguishable in part a.

eter C gives one relationship between b_A and b_B:

$$C = \left(\frac{b_A}{v_A} - \frac{b_B}{v_B}\right)^2 = 4.18 \times 10^{19}\ \mathrm{cm}^{-4} \tag{8}$$

Another relationship between b_A and b_B is obtained from measurements of the density of the dPB[90]-dPB[63] diblock, ρ_d ($\rho_d = 0.9098$ g/cm^3). We also synthesized the hydrogeneous version of this polymer, hPB[90]-hPB[63], using the same polybutadiene sample and measured its density, ρ_h ($\rho_h = 0.8633$ g/cm^3). Using arguments given in ref 7, we obtain $b_A = 2.44 \times 10^{-12}$ cm and $b_B = 3.16 \times 10^{-12}$ cm. (We assume $b_A < b_B$, based on deuteration data on homopolymers.)

The final step of the analysis was a least-squares fit of eq 3 through the data from the A−B melt at each temperature with χ and α as adjustable parameters. In Figure 2a we show the measured coherent SANS profiles $I(q)$ from the A−B diblock copolymer at 29 °C (open squares) along with the results of the RPA fits described above (solid line). It is clear that while the calculated curve explains the presence of the peak in $I(q)$ and the high q portion of the scattering profile rather well, the agreement is not satisfactory in the low q-regime. The theoretical scattering approaches zero at low q while the experimental $I(q)$ data appear to approach a plateau of about 1 cm^{-1} at low q (Figure 2a). Some corrections to the theoretical calculations are necessary due to the finite polydispersity of our samples (see Table 1). This effect was studied by Burger et al.[32] who accounted for chain polydispersity but ignored the possibility of labeling polydispersity. The dashed curve in Figure 2a shows the $I(q)$ computed for polydisperse A−B diblock copolymer melts using the characterization data provided in Table 1. Details of this calculation are given in the appendix. The theoretically calculated curves for polydisperse and monodisperse block copolymers (dashed and solid curves, respectively in Figure 2a) are indistinguishable. It is thus clear that the previous treatment of polydisperse diblock copolymers[32] is incapable of describing the data from our A−B diblock copolymer. The situation becomes worse when one examines data from our A−B copolymer at 102 °C, as shown in Figure 2b. Here the theoretical curves (the solid curve corresponds to the monodisperse calculation and the dashed curve corresponds to the polydisperse calculation) and the experimental data bear little resemblance. The theories predict a well-defined peak in $I(q)$ at finite q whereas the experimental $I(q)$ is a monotonically decreasing function of q. It is clear that a new expression for $I(q)$ is necessary to describe the data in Figure 2. We now describe the derivation of such an expression.

Theory

In the random phase approximation, the coherent scattering intensity from a single-phase, $(n + 1)$ component, incompressible mixture, $I(q)$, is given by[33−36]

$$I(q) = \mathbf{B}^{\mathbf{T}}\, \mathbf{S}(q)\, \mathbf{B} \tag{9}$$

where **B** is an n dimensional column vector whose elements, B_i, are related to the scattering length densities of the components and $\mathbf{S}(q)$ is an n by n structure factor matrix whose elements, S_{ij}, describe correlations between components i and j. A component is defined to be a connected chain of identical monomers. We ignore the fact that the blocks in our system are actually statistical copolymers. This is appropriate because the RPA in polymer mixtures is based on a coarse-grained view of polymer chains, and the monomers interact weakly with each other.[37]

We assume that our mixture is composed of m distinct chemical species, each of which is an A−B block copolymer. We use the subscript k to describe each of these species; $k = 1$ to m. The number of components, n, is thus equal to $2m$. The subscripts i and j in eq 9 take on values between 1 and n. We label the A-block of the kth species as $i = 2k - 1$, the B-block of the kth species as $i = 2k$. Following Hammouda, we incorporate the incompressibility assumption by introducing a “background” component labeled 0.[33]

$$B_i = \frac{b_i}{v_i} - \frac{b_0}{v_0} \tag{10}$$

where b_i is the scattering length of component i, and v_i is the monomer volume of component i.

The structure factor matrix, $\mathbf{S}(q)$, is given by the solution to the following equation:

$$\mathbf{S}(q) = [\mathbf{S}^0(q)^{-1} + \mathbf{V}(q)]^{-1} \tag{11}$$

where the elements of the matrix $\mathbf{S}^0(q)$ describe inter- and intracomponent correlations due to connectivity alone while $\mathbf{V}(q)$ describes the energetic interactions between the components.

We now use the standard approximations of RPA to construct matrices $\mathbf{S}^0(q)$ and $\mathbf{V}(q)$ assuming that the only factor that distinguishes the n components is their extent of deuteration, i.e., their scattering lengths b_i. Without loss of generality, we assume that our monomers occupy a volume $v = 100$ Å^3 (applicable to both A and B blocks and identical to our reference volume). The components of $\mathbf{S}(q)$ are then given by

$$S^0{}_{ii}(q) = N_A\phi_i v P_A(q) \quad \text{(when } i \text{ is odd)} \tag{12}$$

$$S^0{}_{ii}(q) = N_B\phi_i v P_B(q) \quad \text{(when } i \text{ is even)} \tag{13}$$

$$S^0{}_{ij}(q) = S_{ji}{}^0(q) = (N_A\phi_i N_B\phi_j)^{1/2} v F_A(q) F_B(q) \quad \text{(when } j = i + 1,\ i \text{ is odd)} \tag{14}$$

$$\text{otherwise} \quad S^0{}_{ij}(q) = 0 \tag{15}$$

In eqs 12−15, ϕ_i is the volume fraction of component i in the mixture, N_i (i = A or B) is the number of monomers in each block, and $P_i(q)$ and $F_i(q)$ are the familiar Debye and Leibler functions, given by eqs 2 and 6, respectively.

The matrix $\mathbf{V}(q)$, which we now specify, contains information about the background component labeled 0. It is essential that the background component chains are not covalently bonded to any of the n components in the mixture. Since there are no such components in our mixture, the background component in our mixture is a fictitious component. We will ultimately take the limit of our expression with $\phi_0 \to 0$. It is thus convenient to make the background component as simple as possible. We assume that it is a chain with one repeat unit ($N_0 = 1$), that it has a scattering length $b_0 = 0$, and thus $P_0(q) = 1$ (independent of q). The components of matrix $V(q)$ are the following:

$$V_{ij}(q) = V_{ji}(q) = \frac{1}{\phi_0 v} + \frac{\chi}{v} \quad \text{(when } i + j \text{ is odd)} \tag{16}$$

$$V_{ij}(q) = V_{ji}(q) = \frac{1}{\phi_0 v} \quad \text{(when } i + j \text{ is even)} \tag{17}$$

The governing equations (eqs 9−17) are formidable for large m when ϕ_i are unknown, and we were unable to obtain an analytical expression for $I(q)$ that could be applied to block copolymers with arbitrary compositions. However, the block copolymer that we have studied experimentally is nearly symmetric, i.e., to a good approximation

$$N_A = N_B = N \tag{18}$$

which implies that

$$\phi_i = \phi_{i+1} \quad (i \text{ is odd}) \tag{19}$$

$$P_A(q) = P_B(q) = P(q) \tag{20}$$

and

$$F_A(q) = F_B(q) = F(q) \tag{21}$$

Substituting eqs 10−21 into eq 9, conducting the necessary algebraic simplifications, and evaluating I(q) in the $\phi_0 \to 0$ limit, we obtain the following analytical expression for $I(q)$, for $m = 1$ (the trivial case), 2, and 3

$$I(q) = \frac{N}{v}\left\{K_a(F^2(q) + P(q)) - (F^2(q) - P(q)) \times \left[K_b + \frac{K_c}{1 + \frac{\chi N}{2}(F^2(q) - P(q))}\right]\right\} \tag{22}$$

where K_a, K_b, and K_c are q-independent parameters related to the scattering lengths of the components. We used a Mathematica program to perform the symbolic operations and simplifications.

For convenience, we define A_k and B_k to be the scattering lengths of the monomers of the A-block and B-block, respectively, of species k, and the volume fraction of the A-block of the kth species to be f_k ($\sum_{k=1}^{m} f_k = {}^1/_2$). Thus, $A_k = b_{2k-1}$ and $B_k = b_{2k}$ (k takes values from 1 to m), and

$$K_a = \sum_{i=1}^{m}\sum_{j=1}^{m}(A_i - A_j + B_i - B_j)^2 f_i f_j \tag{23}$$

$$K_b = \sum_{i=1}^{m}\sum_{j=1}^{m}(A_i - A_j - B_i + B_j)^2 f_i f_j \tag{24}$$

$$K_c = \left(\sum_{i=1}^{m}(A_i - B_i) f_i\right)^2 \tag{25}$$

If we assume that the deviations in the scattering lengths of each component (δb_{Ai} and δb_{Bi}) about the mean values are uncorrelated, i.e.,

$$b_i = b_A + \delta b_{Ai} \tag{26}$$

and

$$b_{i+1} = b_B + \delta b_{Bi} \tag{27}$$

then

$$K_a = K_b = {}^1/_2(\langle \delta b_A{}^2 \rangle + \langle \delta b_B{}^2 \rangle) \tag{28}$$

where

$$\langle \delta b_j{}^2 \rangle = \frac{\sum_{i=1}^{m} f_i \delta b_{ji}{}^2}{\sum_{i=1}^{m} f_i} \quad (j = A, B)$$

and

$$K_c = K_a/2 + (b_A - b_B)^2/4 \tag{29}$$

and $I(q)$ is given by

$$I(q) = \frac{N}{v}\left\{K_a(F^2(q) + P(q)) - (F^2(q) - P(q)) \times \left[K_a + \frac{K_a/2 + K/4}{1 + \frac{\chi N}{2}(F^2(q) - P(q))}\right]\right\} \quad (30)$$

where K is the average contrast between the blocks

$$K = (b_A - b_B)^2 \quad (31)$$

Equation 30 describes the SANS profiles from symmetric block copolymers with nonuniform deuterium labeling, and it is the main result of our paper. Our result contains one new temperature-independent parameter K_a, which is a measure of the mean deviations of the scattering lengths from the mean values (A and B). Note that $I(q)$ does not depend on the detailed distribution of scattering lengths but on the average value of the deviations of the scattering lengths about their mean values.

All of the symbolic manipulations required to obtain $I(q)$ (substituting the results of eqs 10–21 into eq 9 and evaluating the limit as $\phi_0 \to 0$), were performed on an IBM-compatible personal computing machine, using Mathematica. The program was written for arbitrary m. However, we were only successful in conducting the necessary operations for $m = 1$, 2, and 3. For $m \geq 4$, the memory requirements for the required symbolic manipulations exceeded the available memory on our machine. For the case of $m = 4$, however, we were able to evaluate $I(q)$ using eq 9 for particular values of the parameters (b_i, ϕ_i, P, F, χ, q, etc.). We compared the results of this evaluation with the $I(q)$ obtained using eqs 22–25 and found exact agreement in all cases. We thus have concrete evidence that eqs 22–25 apply to the $m = 4$ case. For the case of $m = 5$, the memory requirements for evaluating $I(q)$ numerically exceeded the available memory on our machine. At this point we have no proof that $I(q)$ obtained from eq 22 is identical to that obtained from eq 9 for all m. Our work thus far, however, strongly suggests that this is the case.

Comparison of Theory and Experiment

In Figure 3, we show data obtained from our sample between 102 °C to 134 °C. It is evident that the experimentally determined $I(q)$ profiles in this range are more or less independent of temperature. In the $\chi \to 0$ limit (i.e., $\chi \ll 10.5/N$), the calculated $I(q)$ (eq 30) also becomes essentially temperature independent.[38] In this limit eq 30 simplifies to eq 32

$$I(q) = \frac{N}{v}\left\{K_a(F^2(q) + P(q)) - (F^2(q) - P(q))\left(\frac{3K_a}{2} + \frac{K}{4}\right)\right\} \quad (32)$$

The curves in Figure 3 are the result of nonlinear least-squares fits of eq 32 through each data set with K_a and K as adjustable parameters. As eqs 30 and 32 apply to the case where the monomer volume is equal to the reference volume, $v = 100$ Å^3, the value of N at each temperature was chosen so that the molecular volume was equal to Nv.[39] The statistical segment lengths obtained from the A/B blend were used at each temperature in this fit.[39] The fit gives $K_a = 4.30 \times 10^{-26}$ cm^2 and $K = 1.86 \times 10^{-25}$ cm^2 (these are the average values of the parameters obtained by fitting the four data sets shown in Figure 3). It is evident that eq 32 captures most of the features seen in the experimental data. In addition, it is clear that the statistical segment lengths obtained from the binary A/B blend are applicable to the A–B block copolymer.

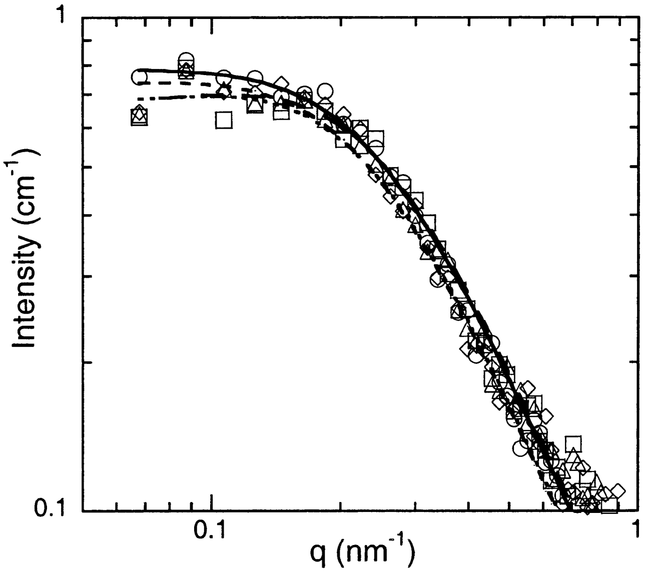

Figure 3. SANS data obtained from the A–B diblock copolymer. The data were taken at the following temperatures: 102 (circles), 113 (squares), 123 (diamonds), and 134 °C (triangles). The solid curves are the random phase approximation for a partially deuterated diblock copolymer fit to the data, simplified for the case when $\chi \to 0$ (solid curve is 102 °C, dashed curve is 113 °C, dot–dashed curve is 123 °C, and dotted curve is 134 °C.

Both $F(q)$ and $P(q)$ approach 1 as $q \to 0$ (eqs 2 and 6). Thus, the value of K_a, the parameter that describes the polydispersity in scattering lengths, is essentially determined by the low-q plateau in $I(q)$ in Figure 3, as $I(q = 0) = 2NK_a/v$ (see eq 32). The parameter K, on the other hand, is determined from the full q dependence of I. This analysis enables a more refined estimate of the mean scattering lengths of the monomers in the block copolymer: $b_A = 2.58 \times 10^{-12}$ cm and $b_B = 3.01 \times 10^{-12}$ cm. These values are within 5% to those obtained earlier (see text after eq 8) where labeling nonuniformity was ignored. Our earlier methods[7] for estimating b_A and b_B are thus surprisingly robust. The new analysis, however, provides a quantitative measure of the deviations of the scattering lengths in our sample from the mean, $\sqrt{\delta b_{Ai}{}^2}/b_A \approx \sqrt{K_a}/b_A = 0.081$. To our knowledge, this is the first estimate of the extent of labeling nonuniformity that is obtained when deuterated diblock copolymers are synthesized by saturating polydiene precursors.

In Figure 4, we show $I(q)$ data obtained from the A–B copolymer at selected temperatures between 29 and 102 °C.[40] The curves through the data are fits of the full expression for $I(q)$ (eq 30) with χ and α as adjustable parameters (in this case $l_{i,\text{ref}}$ is defined as the average binary statistical segment length at 30 °C, 0.66 nm). It is evident that the agreement between the experimental data and eq 30 is excellent over the accessible q and T range. The high-temperature data in Figure 4 has enabled a new "view" of block copolymer chains because

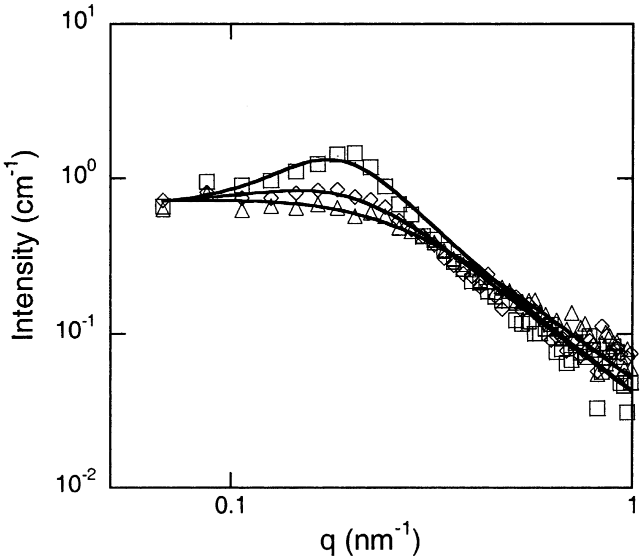

Figure 4. SANS data obtained from the A−B diblock copolymer. The solid curves are the random phase approximation for a partially deuterated diblock copolymer fit to the data (full expression). The data were taken at the following temperatures: 29 (squares), 71 (diamonds), and 113 °C (triangles).

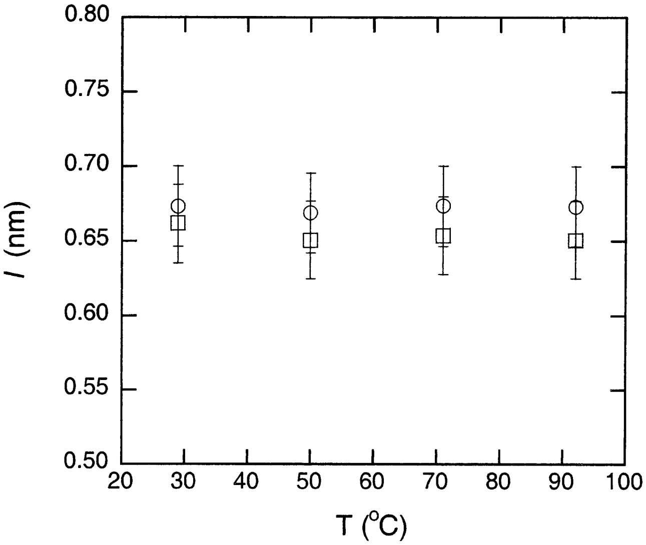

Figure 5. Statistical segment length is shown as a function of temperature as obtained from the SANS data and random phase approximation for binary blends (circles) and partially deuterated diblock copolymers (squares).

we have obtained an estimate of the statistical segment lengths ($l = 0.63$ nm at $T \geq 102$ °C) of our blocks despite the absence of a scattering peak in $I(q)$.

In Figure 5, we compare the values of l obtained from binary A/B blends and our A−B block copolymer. The values of l obtained from these two systems are within experimental error across the accessible T window. In Figure 6, we compare the values of χ obtained from binary A/B blends and our A−B block copolymer. At low temperatures, where the concentration fluctuations contribute substantially to the scattering signal, we observe reasonable agreement between the two data sets. The errors in χ (based on the uncertainty in measured I values) from our block copolymers increase with increasing temperature as the scattering due to concentration fluctuations is overwhelmed by that due to labeling nonuniformity. It is not clear if the deviations between the χ parameters determined from blends and block copolymers at higher temperatures is due to physical effects (e.g., those discussed in ref 32) or small systematic errors due to the relatively weak scattering intensity from our sample (Figure 4).

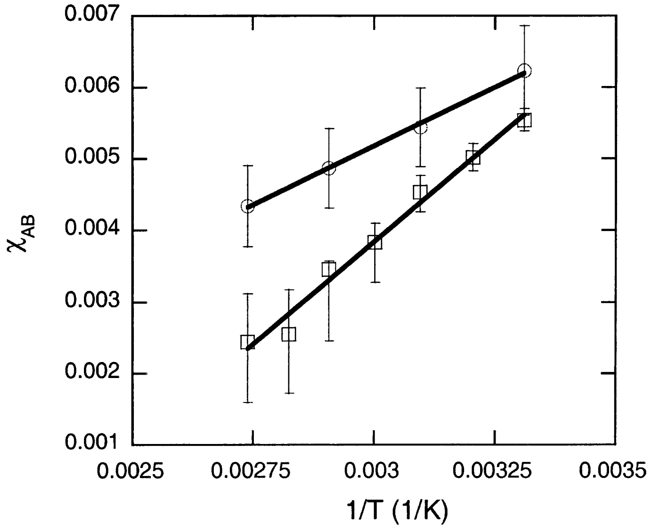

Figure 6. Flory−Huggins parameter, χ, is shown as a function of inverse temperature as obtained from the SANS data and random phase approximation for the binary A/B blend (circles) and the partially deuterated A−B diblock copolymer (squares). The two data sets have been fit to a function of the form $\chi = A + B/T$ (solid lines). The values of the fit parameters are $A = -0.0047$ and $B = 3.29$ (blend) and $A = -0.0133$ and $B = 5.72$ (block copolymer).

We were only able to prove the validity of eq 30 for $m \leq 4$. Despite this limitation, we find quantitative agreement between the experimental data and eqs 30 and 32, as shown in Figures 3 and 4. It is clear that the experimental system is composed of a very large number of chemically distinct species (experimental $m \gg 4$). The agreement between theory and experiment indicates that either m values as small as 4 are adequate for describing our nonuniformly labeled polymers, or that eq 30 is valid for arbitrarily large values of m.

Concluding Remarks

We have derived an expression for $I(q)$ obtained from a symmetric diblock copolymer with nonuniformly labeled blocks. The final expression (eq 30) contains one additional parameter K_a, which is related to the mean square deviations of the scattering lengths of the blocks from their mean value. We have demonstrated the importance of these corrections in analyzing $I(q)$ obtained from a dPB[90]-dPB[63] block copolymer. This polymer was obtained by saturating a polybutadiene block copolymer precursor with deuterium. The deviations in scattering length are a natural consequence of the complex side-reactions that occur during the saturation process. Such block copolymers are often used in thermodynamic studies (e.g. refs 7, 41, and 42).

At high temperatures, $I(q)$ of our block copolymer is a monotonically decreasing function of q. At low temperatures, however, a peak develops at finite q, due to disordered concentration fluctuations. The expression that we have derived for $I(q)$ provides a unified interpretation for both kinds of scattering profiles. The statistical segment lengths obtained from our analysis of our block copolymer are in quantitative agreement with the values of these parameters obtained from independent experiments on a hPB[90]/dPB[63] blend. To our knowledge, this kind of quantitative agreement between statistical segment lengths obtained from binary blends and block copolymers has not been previously reported.

We conclude by noting some of the important differences in the analysis of blends containing nonuniformly labeled homopolymers, developed in ref 25, and the present analysis of nonuniformly labeled block copolymers. There are two important differences in the functional form of $I(q)$ in these two cases.

(1) The structure factor of homopolymer blends[25] with nonuniform labels can be decomposed into two additive parts: one part is identical to the structure factor of uniformly labeled homopolymer blends (the usual RPA formula) while the other contains corrections due to nonuniformity of labeling. This additivity of contributions is convenient because one can simply subtract the contribution of labeling nonuniformity and use the conventional RPA formulas to analyze the data. It is evident from eq 30, that the contribution of labeling nonuniformity to $I(q)$ of block copolymers cannot be expressed as an additive correction to the $I(q)$ obtained from a uniformly labeled block copolymer. There are thus no simple subtraction procedures for correcting for the effect of nonuniform labeling in the case of block copolymers.

(2) For the homopolymer blend case, the m-component RPA equations could be simplified without the help of computer-aided symbolic manipulation. In addition, it was possible to obtain an analytical expression for $I(q)$ that was valid for any blend, regardless of blend composition and component molecular weights. For the block copolymer case, the m-component RPA equations were substantially more challenging, and simplifications were only possible with the help of a symbolic manipulation software package (Mathematica). We have only solved the simplest case of a symmetric block copolymer ($N_A = N_B$), and proof of the validity of our equation could only be constructed for $m \leq 4$. Limited as it is, we hope that this work will serve as a starting point for understanding of the effect of labeling nonuniformity in block copolymers, regardless of composition, and more complex systems such as multicomponent blends containing these block copolymers.

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Appendix:

Burger et al. have developed a correction to the random phase approximation for a diblock copolymer which takes into account the effect of polydispersity in block size on scattering from the disordered state.[32] The expression for $I(q)$ resembles that developed by Leibler;[27] however, the Debye and Leibler functions are replaced by their averages over the various block sizes:

$$I(q) = \left(\frac{b_A}{v_A} - \frac{b_B}{v_B}\right)^2 \left[\frac{S^\circ_{AA} + S^\circ_{BB} + 2S^\circ_{AB}}{S^\circ_{AA}\, S^\circ_{BB} - (S^\circ_{AB})^2} - \frac{2\chi}{v}\right]^{-1}$$

$$S^\circ_{ii} = \phi_i N_i v_i \langle P_i(q)\rangle$$

$$S_{AB} = (\phi_A N_A \mathrm{v}_A \phi_B N_B v_B)^{1/2} \langle F_A(q)\rangle \langle F_B(q)\rangle$$

$$\langle P_i(q)\rangle = \frac{2}{\langle x_i\rangle^2}(\langle \exp(-x_i)\rangle + \langle x_i\rangle - 1) \quad (\mathrm{i} = \mathrm{A, B})$$

$$\langle F_i(q)\rangle = \frac{1 - \langle \exp(-x_i)\rangle}{\langle x_i\rangle} \quad (\mathrm{i} = \mathrm{A, B})$$

$$\langle \exp(-x_i)\rangle = \left(1 + \frac{1}{2} U_A \langle x_i\rangle\right)^{-1/U_A}$$

$$\langle x_i\rangle = \langle N_{ni}\rangle\, b_i^{\,2} q^2/6$$

$$U = \frac{N_w}{N_n} - 1 = U_A/2 = U_B/2$$

where N_n is the number-average degree of polymerization, N_w is the weight-average degree of polymerization, and all other variables have been defined previously.

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